

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C10M 143/08, C10L 3/12, 1/16, C07C 9/16		A1	(11) International Publication Number: WO 99/20720 (43) International Publication Date: 29 April 1999 (29.04.99)
<p>(21) International Application Number: PCT/US98/21766</p> <p>(22) International Filing Date: 15 October 1998 (15.10.98)</p> <p>(30) Priority Data: 60/062,824 20 October 1997 (20.10.97) US</p> <p>(71) Applicant: MOBIL OIL CORPORATION [US/US]; 3225 Gallows Road, Fairfax, VA 22037 (US).</p> <p>(72) Inventors: FORBUS, Thomas, R., Jr.; 30 Two Penny Run, Pilesgrove Township, Woodstown, NJ 08098 (US). JIANG, Zhaozhong; Apartment G-9, 968 Kings Highway, Thoro-fare, NJ 08086 (US). PARTRIDGE, Randall, D.; 229 Mountwell Avenue, Haddonfield, NJ 08033 (US). SCHRAMM, Suzanne, E.; 26 Cherry Circle, Glen Mills, PA 19342 (US). TREWELLA, Jeffrey, C.; 283 Hickory Drive, Kennett Square, PA 19348-1551 (US).</p> <p>(74) Agents: STEINBERG, Thomas, W. et al.; Mobil Oil Corporation, 3225 Gallows Road, Fairfax, VA 22037 (US).</p>		<p>(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).</p> <p>Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>	
<p>(54) Title: ISOPARAFFINIC LUBE BASESTOCK COMPOSITIONS</p> <p>(57) Abstract</p> <p>A liquid hydrocarbon composition, containing paraffinic hydrocarbon components in which the extent of branching, as measured by the percentage of methyl hydrogens (BI), and the proximity of branching, as measured by the percentage of recurring methylene carbons which are four or more carbons removed from an end group or branch ($\text{CH}_2 > 4$), are such that: (a) $\text{BI} - 0.5(\text{CH}_2 > 4) > 15$; and (b) $\text{BI} + 0.85(\text{CH}_2 > 4) < 45$ as measured over said liquid hydrocarbon composition as a whole.</p>			

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GB	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

ISOPARAFFINIC LUBE BASESTOCK COMPOSITIONS

This application claims priority under 35 U.S.C. §119 to U.S. provisional application no. 60/062,824.

5 High performance, lubricating oil basestocks have been developed which posses unique compositional characteristics and which demonstrate superior low temperature performance properties.

10 Premium, high performance, lubricant basestocks generally exhibit useful viscosities over a wide range of temperatures, have improved viscosity index, and demonstrate lubricity, thermal and oxidative stability, and pour point equal to or better than conventional mineral oils. Such advantageous rheological and performance properties enhance their performance in lubricant formulations relative to mineral oil-based formulations, including a wider operating temperature window. However, premium lubricant base stocks are more expensive to produce than conventional mineral oil lubricants.

15 Many researchers have investigated ways of converting relatively low value hydrocarbon feedstocks, such as natural gas, into higher value products, such as fuels and lubricants. Additionally, much investigation has been conducted into catalytically upgrading waxy hydrocarbon feedstocks, which have significant concentrations of straight chain paraffin components, into more useful products by hydroisomerization and dewaxing, processes which 20 isomerize and crack the straight chain paraffin wax components of the feedstock, respectively.

Processes for the production of hydrocarbon fuels and lubricants from synthesis gas, a mixture of hydrogen and carbon monoxide, have been known for some time, and of them, the Fischer-Tropsch (FT) process is probably the best known. An account of the development of the process and its more notable characteristics is given in Kirk-Othmer, *Encyclopedia of 25 Chemical Technology*, Third Edition, John Wiley & Sons, New York, 1980, Vol. 11, pp. 473-478.

In the FT process, synthesis gas, generally formed by partial oxidation of methane, is passed over a catalyst at elevated temperature and pressure to produce a number of carbon monoxide reduction products including hydrocarbons, alcohols, fatty acids and other 30 oxygenated compounds. In favorable circumstances, oxygenated materials can comprise less than 1 percent of a total desired liquid product. The hydrocarbon product is highly paraffinic in

nature and typically includes hydrocarbon gas, light olefins, gasoline, light and heavy fuel oils and waxy gas oils. Because the higher boiling fractions in the product are generally too waxy for general use either as liquid fuels or lubricants, further processing or upgrading is normally necessary before they can be used, either as such or by being added to the general pool of

5 products. Advantageously, the FT products contain little, if any, of typical petroleum contaminants, such as aromatic compounds, cycloparaffinic compounds (naphthenes), sulfur compounds and nitrogen compounds, due to the relatively pure nature of the feedstocks: hydrogen and carbon monoxide, and ultimately, methane or natural gas.

U.S. Patent no. 4,500,417 discloses conversion of the high boiling fraction of FT

10 products by contact with a high-silica, large pore zeolite and a hydrogenation component to produce a distillate fraction and a lube fraction characterized by a high VI (viscosity index) and low pour point. Catalysts include zeolite Y, zeolite Beta, mordenite, ZSM-3, ZSM-4, ZSM-18 and ZSM-20.

U.S. Patent no. 4,906,350 discloses a process for the preparation of a lubricating base

15 oil with a high VI and a low pour point by catalytic dewaxing at least part of the hydrocrackate of a wax-containing mineral oil fraction over a zeolitic catalyst selected from among ZSM-5, ZSM-11, ZSM-23, ZSM-35, ZSM-12, ZSM-38, ZSM-48, offretite, ferrierite, zeolite beta, zeolite theta, zeolite alpha and mixtures thereof.

U.S. Patent no. 4,943,672 discloses a process for hydroisomerizing FT wax to produce

20 lubricating oil having a high VI and a low pour point by first hydrotreating the wax under relatively severe conditions and thereafter hydroisomerizing the hydrotreated wax in the presence of hydrogen on a particular fluorided Group VIII metal-on-alumina catalyst.

U.S. Patent no. 5,059,299 discloses a method for isomerizing slack wax obtained from mineral oils and wax to form high VI, very low pour point lube oil basestocks by isomerizing

25 over a Group VI-VIII on halogenated refractory metal oxide support catalyst, followed by solvent dewaxing.

U.S. Patent nos. 5,135,638 and 5,246,566 disclose wax isomerization processes for

producing lube oil having excellent viscosity, VI and low pour point by isomerizing a waxy

petroleum feed over a molecular sieve having certain pore measurements and at least one Group

30 VIII metal. Catalysts include SAPO-11, SAPO-31, SAPO-41, ZSM-22, ZSM-23 and ZSM-35.

U.S. Patent no. 5,282,958 discloses a process for dewaxing a hydrocarbon feed including straight chain and slightly branched paraffins having 10 or more carbon atoms to produce a dewaxed lube oil using catalysts of a specified pore geometry and containing at least one Group VIII metal. The feedstock is contacted with the catalyst in the presence of 5 hydrogen; exemplified catalysts include SSZ-32, ZSM-22 and ZSM-23.

U.S. Patent no. 5,306,860 discloses a method of hydroisomerizing FT-derived paraffins over a series of catalysts, including a zeolite Y catalyst to form high VI, low pour point lube oils.

10 U.S. Patent no. 5,362,378 discloses conversion of FT heavy end products with a platinum/boron-zeolite Beta catalyst having a low alpha activity to produce an extra high VI lube, which may then be dewaxed by conventional solvent dewaxing or by increasing the severity of the hydroisomerization step.

15 European Patent no. 0 776 959 A2 discloses a process for preparing lubricating base oils having a VI of at least 150 from a FT wax feed by first hydroisomerizing over a suitable catalyst in the presence of hydrogen and then either solvent or catalytically dewaxing the intermediate 390°C+ fraction.

20 However, none of the references discussed above disclose or suggest preparation of liquid hydrocarbons of a specific and limited range of compositions having any particular combination of branching properties, which lead to highly desirable lubricating properties including an unexpected combination of high viscosity index and low pour point. In fact, none 25 of the cited references even discloses or suggests measuring Branching Index (BI) or Branching Proximity, as discussed below.

U.S. Patent no. 4,827,064 discloses high VI synthetic lubricant compositions of polyalphaolefins wherein a "branching ratio", CH_3/CH_2 , is measured.

25 The disclosures of the U.S. patents described above are hereby incorporated by reference in their entireties.

A first object of the present invention is production of unique liquid hydrocarbon composition which may be useful as lubricant oil basestocks having useful low temperature viscometric properties.

Another object of the present invention is to provide an outlet for low value natural gas, by converting it to premium value lubricant basestocks by a combination of Fischer Tropsch synthesis, hydroisomerization and catalytic dewaxing steps.

One embodiment of the present invention is directed to a liquid hydrocarbon composition of paraffinic hydrocarbon components in which the extent of branching, as measured by the percentage of methyl hydrogens (BI), and the proximity of branching (or "Branching Proximity"), as measured by the percentage of recurring methylene carbons which are four or more carbons removed from an end group or branch ($\text{CH}_2 > 4$), are such that:

- 5 (a) $\text{BI} - 0.5(\text{CH}_2 > 4) > 15$; and
- 10 (b) $\text{BI} + 0.85(\text{CH}_2 > 4) < 45$;

as measured over the liquid hydrocarbon composition as a whole.

Another embodiment of the present invention is directed to a lubricant oil basestock composition having paraffinic hydrocarbon components in which the extent of branching, as measured by the percentage of methyl hydrogens (BI), and the proximity of branching, as measured by the percentage of recurring methylene carbons which are four or more carbons removed from an end group or branch ($\text{CH}_2 > 4$), are such that:

- 15 (a) $\text{BI} - 0.5(\text{CH}_2 > 4) > 15$; and
- (b) $\text{BI} + 0.85(\text{CH}_2 > 4) < 45$;

as measured over the lubricant oil basestock composition as a whole.

20 In another embodiment, the present invention is directed to a lubricating oil composition of a liquid hydrocarbon composition having paraffinic hydrocarbon components in which the extent of branching, as measured by the percentage of methyl hydrogens (BI), and the proximity of branching, as measured by the percentage of recurring methylene carbons which are four or more carbons removed from an end group or branch ($\text{CH}_2 > 4$), are such that:

- 25 (a) $\text{BI} - 0.5(\text{CH}_2 > 4) > 15$; and
- (b) $\text{BI} + 0.85(\text{CH}_2 > 4) < 45$;

as measured over the liquid hydrocarbon composition as a whole, and optionally, effective amounts of lubricating oil additives such as, but not limited to, antioxidants, anti-wear additives, extreme pressure additives, friction modifiers, viscosity index improvers, pour point depressants, detergents, dispersants, corrosion inhibitors, metal deactivators, seal compatibility additives, demulsifiers, anti-foam additives, and mixtures thereof.

The above and other objects, features and advantages of the present invention will be better understood from the following detailed descriptions, taken in conjunction with the accompanying drawings, all of which are given by illustration only, and are not limitative of the present invention.

5 Figure 1 is a graph comparing the low temperature viscometric properties of the liquid hydrocarbon compositions of the present invention with a typical hydroprocessed lubricant basestocks.

10 Figure 2 is a graph mathematically illustrating the structural limitations of BI and $\text{CH}_2>4$, as set forth in formulae (a) and (b), which define the limits of the inventive compositions disclosed herein.

Figure 3 is a graphic comparison of the dynamic viscosities (DV@-40°C), measured by the CCS method ASTM D5392, and the kinematic viscosities (KV@100°C) of various hydrocarbon fluids, including those of the present invention.

15 Further scope of applicability of the present invention will become apparent from the detailed description given hereinafter. However, it should be understood that the detailed description and specific examples, while indicating preferred embodiments of the invention, are given by way of illustration only, since various changes and modifications within the spirit and scope of the invention will become apparent to those skilled in the art from this detailed description.

20 One embodiment of the present invention is directed to a liquid hydrocarbon composition of paraffinic hydrocarbon components in which the extent of branching, as measured by the percentage of methyl hydrogens (BI), and the proximity of branching, as measured by the percentage of recurring methylene carbons which are four or more carbons removed from an end group or branch ($\text{CH}_2>4$), are such that:

25 (a) $\text{BI} - 0.5(\text{CH}_2>4) > 15$; and
(b) $\text{BI} + 0.85(\text{CH}_2>4) < 45$;

as measured over the liquid hydrocarbon composition as a whole.

30 The hydrocarbon fluids of the present invention preferably have BI greater than or equal to 25.4, and Branching Proximities ($\text{CH}_2>4$) less than or equal to 22.5, although any composition meeting the limitations of formulae (a) and (b) is intended to be within the scope of the present invention.

Measurement of the branching characteristics of the liquid hydrocarbons according to the present invention was performed by nuclear magnetic resonance (NMR) analysis, and is described in more detail below.

The liquid hydrocarbon composition of the present invention may have very low 5 concentration levels of typical contaminants found in lube oil basestocks refined from natural mineral oils, depending upon the nature of the feedstock used to produce the liquid hydrocarbons. Typically, the liquid hydrocarbon compositions of the present invention have less than 0.1 wt% aromatic hydrocarbons, less than 20 ppm by weight of nitrogen-containing compounds, less than 20 ppm by weight of sulfur-containing compounds and low levels of 10 naphthenic hydrocarbons, i.e. cycloparaffins. It is expected that the levels of these contaminants may be much lower, or that they may be entirely absent from the inventive liquid hydrocarbons. Accordingly, the concentration levels of both sulfur and nitrogen compounds in the inventive hydrocarbon compositions, when derived from FT waxes, are preferably less than 10 ppm each, and more preferably less than 1 ppm each.

15 The low levels of sulfur- and nitrogen-containing compounds are primarily due to the nature of the feedstock. Use of Fischer-Tropsch waxes, formed from relatively pure synthesis gas mixtures which have little, if any, nitrogen- or sulfur-containing compounds in the gas phase results in hydrocarbon fluids having very low levels of typical contaminants. In contrast, naturally occurring mineral oils have substantial concentrations of organic sulfur and nitrogen 20 compounds, which are difficult or impossible to remove by commercial physical separation techniques, such as distillation.

The reasons for the low levels of aromatics and naphthenics in the liquid hydrocarbons of the present invention are two-fold: First, Fischer-Tropsch derived feedstocks are inherently low in ring-containing molecules, as the conversion process produces primarily, and almost 25 exclusively, linear carbon chains; second, careful selection of the hydrocarbon conversion catalysts and conditions used in the process of forming the present invention materials greatly reduces the formation of aromatics and naphthenes during hydroisomerization and catalytic dewaxing.

30 While it is preferable to produce the liquid hydrocarbons of the present invention from Fischer-Tropsch-derived materials in order to obtain the very low level of contaminants in the product fluids, other waxy hydrocarbon materials, such as conventional waxy lube raffinates,

slack waxes, deoiled slack waxes, foot oils and lube distillate hydrocrackates may be used to form the hydrocarbon compositions of the present invention.

On average, the liquid hydrocarbon compositions of the present invention are paraffinic hydrocarbon components having fewer than 10 hexyl- or longer branches per 100 carbon atoms.

5 Likewise, the liquid hydrocarbon compositions of the present invention are paraffinic hydrocarbon components having on average more than 16 methyl branches per 100 carbon atoms. The hydrodewaxing step used to produce the liquid hydrocarbons of the present invention results in significant levels of isomerization of the long chain paraffins in the waxy feedstocks, resulting in paraffinic hydrocarbon components with a plurality of branches, as 10 described in formulae (a) and (b).

The hydrocarbon fluids of the present invention find use as lubricant oil basestocks, or as components of formulated lubricating oils, i.e. in combination with other lubricating oil basestocks, such as for example mineral oils, polyalphaolefins, esters, polyalkylenes, alkylated aromatics, hydrocrackates and solvent-refined basestocks.

15 In another embodiment, the present invention is directed to a lubricant oil basestock composition having paraffinic hydrocarbon components in which the extent of branching, as measured by the percentage of methyl hydrogens (BI), and the proximity of branching, as measured by the percentage of recurring methylene carbons which are four or more carbons removed from an end group or branch ($\text{CH}_2>4$), are such that:

20 (a) $\text{BI} - 0.5(\text{CH}_2>4) > 15$; and
(b) $\text{BI} + 0.85(\text{CH}_2>4) < 45$;

as measured over the lubricant oil basestock composition as a whole.

The lubricant oil basestocks of the present invention contain primarily isoparaffinic components with nominal boiling points of $370^\circ\text{C}+$ and are unusual in that they 25 unexpectedly exhibit a unique combination of both high viscosity indices and extremely low pour points. These two characteristics are generally known in the art to be related in direct proportion, i.e. lowering the pour point of a hydrocarbon fluid results in decreasing the viscosity index, and therefore it is quite unusual to obtain both an extremely low pour point and a relatively high VI in the same fluid. For example, conventional mineral oil basestocks, such as 30 Comparative Examples 3-5 herein, exhibit relatively low VI's when pushed into the low pour point ranges (Table 1).

However, the basestocks of the present invention are characterized by extremely low pour points (PP) of less than or equal to -18°C, preferably less than or equal to -30°C and more preferably less than or equal to -40°C, with kinematic viscosities (KV) ranging from 2.0 cSt to greater than 13 cSt, preferably 4 cSt to 8 cSt, at 100°C and high viscosity indices (VI) from 5 130-165, preferably from 140-165 and more preferably from 150-165, as well as BI and CH₂>4 values as set forth in formulae (a) and (b), above.

In particular, preferred products of the present invention are lubricant oil basestocks having a combination of VI and pour point from 130 VI/-66°C to 165 VI/-27°C and more preferably from 144 VI/-40°C to 165 VI/-27°C.

10 Hydrocarbon conversion catalysts useful in the conversion of the waxy feedstocks disclosed herein to form the hydrocarbon components of the present invention are zeolite catalysts, such as ZSM-5, ZSM-11, ZSM-23, ZSM-35, ZSM-12, ZSM-38, ZSM-48, offretite, ferrierite, zeolite beta, zeolite theta, zeolite alpha, as disclosed in U.S. Patent no. 4,906,350. These catalysts are used in combination with Group VIII metals, in particular palladium or 15 platinum. The Group VIII metals may be incorporated into the zeolite catalysts by conventional techniques, such as ion exchange.

20 The process of making the lubricant oil basestocks of the present invention may be characterized as a hydrodewaxing processes. The hydrodewaxing process may be conducted over a combination of catalysts, or over a single catalyst. Conversion temperatures may range from 200°C to 500°C at pressures ranging from 500 to 20,000 kPa. This process is operated in the presence of hydrogen and hydrogen partial pressures will normally be from 600 to 6000 kPa. The ratio of hydrogen to the hydrocarbon feedstock (hydrogen circulation rate) will normally be from 10 to 3500 n.l.l.⁻¹ (56 to 19,660 SCF/bbl) and the space velocity of the feedstock will normally be from 0.1 to 20 LHSV, preferably 0.1 to 10 LHSV.

25 For example, conversion of the waxy feedstock may be conducted over a combination of Pt/zeolite Beta and Pt/ZSM-23 catalysts in the presence of hydrogen. Alternatively, the process of the producing the inventive lubricant oil basestocks may comprise hydroisomerization and dewaxing over a single catalyst, such as Pt/ZSM-35. In either case, the unique products of the present invention may be obtained.

30 In another embodiment, the present invention is directed to a lubricating oil composition of a liquid hydrocarbon composition having paraffinic hydrocarbon components in which the

extent of branching, as measured by the percentage of methyl hydrogens (BI), and the proximity of branching, as measured by the percentage of recurring methylene carbons which are four or more carbons removed from an end group or branch ($\text{CH}_2 > 4$), are such that:

- (a) $\text{BI} - 0.5(\text{CH}_2 > 4) > 15$; and
- 5 (b) $\text{BI} + 0.85(\text{CH}_2 > 4) < 45$;

as measured over the liquid hydrocarbon composition as a whole, and optionally, effective amounts of lubricating oil additives, such as for example antioxidants, anti-wear additives, extreme pressure additives, friction modifiers, viscosity index improvers, pour point depressants, detergents, dispersants, corrosion inhibitors, metal deactivators, seal compatibility additives, demulsifiers, anti-foam additives, and mixtures thereof.

10 A survey of conventional lubricant additives is provided in Lubricants and Related Products, by Dieter Klamann, in Chapter 9, pp. 177-217, Verlag Chemie GmbH (1984), which indicates some suitable antioxidants as phenolic or aromatic amines; as anti-rust additives benzotriazoles; metal deactivators such as ethylenediamines and imidazoles; VI improvers such 15 as polyisobutenes and polymethacrylates; pour point depressants such as long-chain alkyl phenols and phthalic acid dialkylaryl esters. As dispersants, for example, poly-alkylene succinimides are disclosed; as detergents, compounds such as sulfonates, phenates, sulfurized phenates, phosphates and the like are disclosed. Also disclosed is the use of anti-wear agents and of extreme pressure additives, which may include organic sulfides, metal dithiocarbamates, 20 chlorinated paraffins and organic phosphorous compounds, such as metal dithiophosphates; friction modifiers such as long-chain fatty acids, fatty alcohols and fatty esters; as antifoam additives, polydimethylsiloxanes and polyethylene glycol ethers and esters are known; as seal compatibility additives compounds such as aromatics, aldehydes, ketones and esters; as demulsifiers, dinonylnaphthalenesulfonates are known; and as corrosion inhibitors, tertiary 25 amines, fatty acid amides, phosphoric acid derivatives and sulfonic acids are examples. The skilled artisan will be aware that many other such additive compounds are known in the art and might be useful with the base oils of the present invention.

30 The lubricating oil compositions of the present invention may contain other lubricating oil basestocks, such as mineral oils, polyalphaolefins, esters, polyalkylenes, alkylated aromatics, hydrocrackates and solvent-refined basestocks, in combination with the paraffinic hydrocarbon components described herein. The paraffinic hydrocarbon compositions of the present invention

may be used as the majority base oil for a lubricating oil composition, with other more conventional lube oil basestocks added thereto, or may be used as an additive in combination with a major amount of another lube oil basestock. However, it is preferred that the liquid hydrocarbon compositions of the present invention be present at concentration levels of at least 5 wt% of the total lubricating basestock composition.

EXAMPLES

In the following examples, hydroisomerization and catalytic dewaxing reaction conditions were varied to obtain the desired products, with typical conditions ranging from, but not limited to, 200-370°C, 400-2000 psig, 0.50-2.0 hr⁻¹ LHSV, and 1900-5000 scf/B (standard 10 cubic feet per barrel) H₂ at the reactor inlet.

Lube Basestock Physical Properties

Examples 1-4

A hydrogenated Fischer-Tropsch wax (Paraflint 80) was hydrodewaxed in the presence of hydrogen over a combination of Pt/zeolite Beta hydroisomerization catalyst and Pt/ZSM-23 15 selective dewaxing catalyst. Four different hydrocarbon fluids were obtained under increasingly severe processing conditions, having KV, VI and PP values as indicated in Table 1. Example 4 is an example of the present invention.

Examples 5 and 6

A hydrogenated and partially isomerized Middle Distillate Synthesis Waxy Raffinate 20 (Shell MDS or "SMDS") was hydrodewaxed in the presence of hydrogen over the combination of catalysts used in Examples 1-4. Two different hydrocarbon fluids were obtained under increasingly severe processing conditions, having KV, VI and PP values as indicated in Table 1. Example 6 is an example of the present invention.

Examples 7-9

The Shell MDS feedstock of Examples 5 and 6 was hydrodewaxed over synthetic 25 ferrierite in the presence of hydrogen, under varying severity conditions to produce three different hydrocarbon fluids, having KV, VI and PP values as indicated in Table 1. Examples 7-9 are all examples of the present invention.

Example 10

The waxy feedstock used in Examples 1-4 was hydrodewaxed over Pt/ZSM-48 in the presence of hydrogen to produce a hydrocarbon fluid having the KV, VI and PP values indicated in Table 1. Example 10 is an example of the present invention.

Comparative Examples 1, 2, and 6

5 Commercially prepared polyalphaolefin basestocks of 3.87 cSt and 5.51 cSt KV at 100°C are characterized by pour points of <-65°C and VI's of 130 (Comparative Example 1) and 135 (Comparative Example 2), respectively. A commercial, higher viscosity grade of polyalphaolefin, 150 cSt KV at 100°C, is also included (Comparative Example 6).

Comparative Examples 3-5

10 Several commercially prepared basestocks derived from hydrocracked crude oil fractions were also evaluated. These included: A -18°C pour point, 5.1 cSt KV@100°C, 147 VI Shell XHVI basestock derived from hydroisomerization of slackwax (Comparative Example 3); a 4.0 cSt KV@100°C, 114 VI Yukong 100N basestock, characterized by a pour point of -15°C (Comparative Example 4); and a 6.9 cSt KV@100°C, 102 VI Chevron RLOP 240N basestock, 15 also characterized by a pour point of -15°C (Comparative Example 5).

Typical physical properties of various commercial lube basestocks are compared with those of the inventive ULPP (ultra-low pour point) FT isomerates in Table 1, below.

TABLE 1
BASESTOCK PROPERTIES

Description	Kinematic Viscosity cSt@100°C,	Viscosity Index	Pour Point, °C
Parafin C80 Wax (Feed)	9.42	-	83
Ex. 1	7.14	177	12
Ex. 2	6.52	171	-3
Ex. 3	5.72	161	-24
Ex. 4*	5.54	145	-63
SMDS Waxy Raffinate (Feed)	5.07	-	39
Ex. 5	5.23	142	-24
Ex. 6*	5.11	130	-66
Ex. 7*	5.33	149	-18
Ex. 8*	5.23	136	-59
Ex. 9*	5.46	144	-40
Ex. 10*	7.9	157	-42
Comparative Examples			
C.E. 1	3.87	130	<-65
C.E. 2	5.51	135	<-65
C.E. 3	5.06	147	-18
C.E. 4	4.00	114	-15
C.E. 5	6.94	102	-15
C.E. 6	150	214	-42

* Examples of the present invention

Figure 1 is a graphic comparison of the Cold Crank Simulation (CCS) performances of a typical hydroprocessed hydrocarbon lube basestock (XHVI) and two basestocks according to the present invention. CCS testing was conducted according to ASTM method D5392, which is used to measure the apparent viscosity of motor oils. The CCS viscometer measures the 5 dynamic viscosity of fluids at low temperature and low shear rate and stress, thus simulating the flow of oil in an engine crankcase at low temperature starting (cranking) conditions. The data of Figure 1 demonstrates that the lubricant basestocks of the present invention have superior low temperature viscometric properties.

Measurement of Branching Characteristics

10 **Branching Index (BI)**

For each basestock indicated in Table 1, 359.88 MHz ^1H solution NMR spectra were obtained on a Bruker 360 MHz AMX spectrometer using 10% solutions in CDCl_3 . TMS was the internal chemical shift reference. CDCl_3 solvent gives a peak located at 7.28. All spectra were obtained under quantitative conditions using 90 degree pulse (10.9 μs), a pulse delay time 15 of 30 s, which is at least five times the longest hydrogen spin-lattice relaxation time (T_1), and 120 scans to ensure good signal-to-noise ratios.

H atom types were defined according to the following regions:

9.2-6.2 ppm hydrogens on aromatic rings;
6.2-4.0 ppm hydrogens on olefinic carbon atoms;
20 4.0-2.1 ppm benzylic hydrogens at the α -position to aromatic rings;
2.1-1.4 ppm paraffinic CH methine hydrogens;
1.4-1.05 ppm paraffinic CH_2 methylene hydrogens;
1.05-0.5 ppm paraffinic CH_3 methyl hydrogens.

The branching index (BI) was calculated as the ratio in percent of non-benzylic methyl 25 hydrogens in the range of 0.5 to 1.05 ppm, to the total non-benzylic aliphatic hydrogens in the range of 0.5 to 2.1 ppm. Results from these ^1H NMR analyses are summarized in Table 2 below.

TABLE 2

% Different Types of H from ^1H NMR				
Description	% CH ₃	% CH ₂	% CH	BI
Paraffin C80 Wax (Feed)				
Ex. 1	19.4	78.5	2.1	19.4
Ex. 2	22.3	76	1.7	22.3
Ex. 3	25.6	71.8	2.6	25.6
Ex. 4*	27.6	68.1	4.3	27.6
SMDS Waxy Raffinate (Feed)	10.3	89.7	0	10.3
Ex. 5	23.6	70.1	6.3	23.6
Ex. 6*	29.8	67.8	2.4	29.8
Ex. 7*	26.2	71.2	2.6	26.2
Ex. 8*	30	67	3	30
Ex. 9*	27.9	69.9	2.2	27.9
Ex. 10*	27	70.8	2.2	27
Comparative Examples				
C.E. 1	22.7	74.8	2.5	22.7
C.E. 2	23.4	74.3	2.3	23.4
C.E. 3	26.9	69.4	3.7	26.9
C.E. 4	30.0	61.9	8.1	30.0
C.E. 5	31.5	55.3	13.2	31.5
C.E. 6	19.4	78.7	1.9	19.4

*Examples of the present invention

5 Branching Proximity (CH₂>4)

For each basestock indicated in Table 1, 90.5 MHz ^{13}C NMR single pulse and 135 Distortionless Enhancement by Polarization Transfer (DEPT) NMR spectra were obtained on a Bruker 360 MHz AMX spectrometer using 10% solutions in CDCl_3 . TMS was the internal chemical shift reference. CDCl_3 solvent gives a triplet located at 77.23 ppm in the ^{13}C spectrum. All single pulse spectra were obtained under quantitative conditions using 45 degree pulses (6.3 μs), a pulse delay time of 60 s, which is at least five times the longest carbon spin-lattice relaxation time (T_1), to ensure complete relaxation of the sample, 200 scans to ensure good signal-to-noise ratios, and WALTZ-16 proton decoupling.

The C atom types CH₃, CH₂, and CH were identified from the 135 DEPT ^{13}C NMR experiment. A major CH₂ resonance in all ^{13}C NMR spectra at ~29.8 ppm is due to equivalent recurring methylene carbons which are four or more removed from an end group or branch (CH₂>4). The types of branches were determined based primarily on the ^{13}C chemical shifts for the methyl carbon at the end of the branch or the methylene carbon one removed from the methyl on the branch. The proximity of branches, as indicated by CH₂>4, and the type of carbons are summarized in Table 3.

TABLE 3

% Different Types of C from ^{13}C NMR				
Description	%CH ₃	%CH ₂	%CH	%CH ₂ >4
Parafin C80 Wax (Feed)				
Ex. 1	13.6	81.3	5.1	38.2
Ex. 2	15.7	78.6	5.7	28.8
Ex. 3	17.3	76.3	6.3	22.5
Ex. 4*	18	75.5	6.5	14.7
SMDS Waxy Raffinate (Feed)	6.2	93.8	0	58.8
Ex. 5	16.6	77.3	6	17.3
Ex. 6*	24.9	67.4	7.7	7.7
Ex. 7*	16.4	77.5	6.1	21.8
Ex. 8*	19.3	75.1	5.6	12.8
Ex. 9*	18.1	76.3	5.6	17.7
Ex. 10*	15.9	76.3	7.7	20.5
Comparative Examples				
C.E. 1	11.4	83.7	4.9	20.4
C.E. 2	13.2	81	5.8	20.6
C.E. 3	19	74.3	6.7	22.6
C.E. 4	16.7	72.3	11	20.4
C.E. 5	16.5	62	21.5	19.2
C.E. 6	12.3	83.9	3.8	17.3

* Examples of the present invention

The branching characteristics and pour points of the isoparaffinic components of the 5 exemplary basestocks, as disclosed in Tables 1-3, are compared in the following Table 4.

TABLE 4

Comparison of Isoparaffinic Lube Compositions			
Description	BI	% CH ₂ >4	Pour Point, °C
Parafin C80 Wax (Feed)			83
Ex. 1	19.4	38.2	12
Ex. 2	22.3	28.8	-3
Ex. 3	25.6	22.5	-24
Ex. 4*	27.6	14.7	-63
SMDS Waxy Raffinate (Feed)	10.3	58.8	39
Ex. 5	23.6	17.3	-24
Ex. 6*	29.8	7.7	-66
Ex. 7*	26.2	21.8	-18
Ex. 8*	30	12.8	-59
Ex. 9*	27.9	17.7	-40
Ex. 10*	27	20.5	-42
Comparative Examples			
C.E. 1	22.7	20.4	<-65
C.E. 2	23.4	20.6	<-65
C.E. 3	26.9	22.6	-18
C.E. 4	30.0	20.4	-15
C.E. 5	31.5	19.2	-15
C.E. 6	19.4	17.3	-42

* Examples of the present invention

The basestocks of the present invention can be differentiated from other hydrocarbon basestocks by the extent of branching as indicated by BI and the Branching Proximity as indicated by $\text{CH}_2 > 4$. These compositional fingerprints are graphed to aid in defining unique regions in this 2-dimensional composition space as illustrated in Figure 2 (left quadrant).

5 From Figure 2 it is clear that the branching characteristics of the isoparaffinic basestock compositions of the present invention are within a unique region. Specifically, the composition can be described as comprising mixtures of paraffinic hydrocarbon components in which the extent of branching, as measured by the percentage of methyl hydrogens (BI), and the proximity of branching, as measured by the percentage of recurring methylene carbons which are four or 10 more removed from an end group or branch ($\text{CH}_2 > 4$), are such that:

- a) $\text{BI} - 0.5 (\text{CH}_2 > 4) > 15$; and
- b) $\text{BI} + 0.85 (\text{CH}_2 > 4) < 45$.

15 Figure 3 is a graphic comparison of the dynamic viscosities ($\text{DV}@-40^\circ\text{C}$), measured by the CCS method, and the kinematic viscosities ($\text{KV}@100^\circ\text{C}$) of various hydrocarbon fluids, including those of the present invention. The fluids of the present invention are indicated as 15 "FTWI" (Fischer Tropsch Wax Isomeric), while those conventional hydrocracked stocks are indicated as "HDC". In particular, the HDC data points represent Comparative Examples 3-5 of the present specification.

20 It is clear from the data set forth in Figure 3 that the FWTI fluids of the present invention have significantly improved low-temperature viscosity characteristics compared to that of conventional HDC fluids of the prior art. Note that all of the liquid hydrocarbon fluids of the present invention fall below the dotted line on the graph and can therefore be described by the following equation:

$$(c) \quad \text{DV}_{-40^\circ\text{C}} < 2900(\text{KV}_{100^\circ\text{C}}) - 7000.$$

25 The invention being thus described, it will be obvious that the same may be varied in many ways. Such variations are not to be regarded as a departure from the spirit and scope of the invention, and all such modifications as would be obvious to one skilled in the art are intended to be included within the scope of the following claims.

Claims:

1. A liquid hydrocarbon composition, comprising paraffinic hydrocarbon components in which the extent of branching, as measured by the percentage of methyl hydrogens (BI), and the proximity of branching, as measured by the percentage of recurring methylene carbons which are four or more carbons removed from an end group or branch ($\text{CH}_2 > 4$), are such that:
 - (a) $\text{BI} - 0.5(\text{CH}_2 > 4) > 15$; and
 - (b) $\text{BI} + 0.85(\text{CH}_2 > 4) < 45$;as measured over said liquid hydrocarbon composition as a whole.
- 10 2. The liquid hydrocarbon composition according to claim 1, which contains:
 - less than 0.1 wt% aromatic hydrocarbons;
 - less than 20 ppm (wt) nitrogen-containing compounds; and
 - less than 20 ppm (wt) sulfur-containing compounds.
- 15 3. The liquid hydrocarbon composition according to claim 1, wherein the pour point of the composition is less than -18°C.
4. The liquid hydrocarbon composition according to claim 3, wherein the pour point of the composition is less than -30°C.
5. The liquid hydrocarbon composition according to claim 1, wherein said paraffinic hydrocarbon components have $\text{BI} \geq 25.4$ and $(\text{CH}_2 > 4) \leq 22.5$.
- 20 6. The liquid hydrocarbon composition according to claim 1, wherein said paraffinic hydrocarbon components have nominal boiling points of 370°C+.
7. The liquid hydrocarbon composition according to claim 1, wherein said paraffinic hydrocarbon components comprise on average fewer than 10 hexyl- or longer branches per 100 carbon atoms.
- 25 8. The liquid hydrocarbon composition according to claim 1, wherein said paraffinic hydrocarbon components comprise on average more than 16 methyl branches per 100 carbon atoms.
9. The liquid hydrocarbon composition according to claim 1, wherein the combination of dynamic viscosity, as measured by CCS at -40°C, and kinetic viscosity as measured at 100°C of
- 30 said liquid hydrocarbon fluid are represented by the formula:
 - (c) $\text{DV}_{-40^\circ\text{C}} < 2900(\text{KV}_{100^\circ\text{C}}) - 7000$.

10. A lubricant basestock composition, comprising paraffinic hydrocarbon components in which the extent of branching, as measured by the percentage of methyl hydrogens (BI), and the proximity of branching, as measured by the percentage of recurring methylene carbons which are four or more carbons removed from an end group or branch ($\text{CH}_2>4$), are such that:

5 (a) $\text{BI} - 0.5(\text{CH}_2>4) > 15$; and—
(b) $\text{BI} + 0.85(\text{CH}_2>4) < 45$;

as measured over said lubricant basestock composition as a whole.

11. The lubricant basestock composition according to claim 10, which contains:

less than 0.1 wt% aromatic hydrocarbons;
10 less than 20 ppm (wt) nitrogen-containing compounds; and
less than 20 ppm (wt) sulfur-containing compounds.

12. The lubricant basestock composition according to claim 10, wherein the pour point of the composition is less than -18°C .

13. The lubricant basestock composition according to claim 12, wherein the pour point of the composition is less than -30°C .

14. The lubricant basestock composition according to claim 10, wherein said paraffinic hydrocarbon components have $\text{BI} \geq 25.4$ and $(\text{CH}_2>4) \leq 22.5$.

15. The lubricant basestock composition according to claim 10, wherein said paraffinic hydrocarbon components have nominal boiling points of $370^\circ\text{C}+$.

20 16. The lubricant basestock composition according to claim 10, wherein said paraffinic hydrocarbon components comprise on average fewer than 10 hexyl- or longer branches per 100 carbon atoms.

17. The lubricant basestock composition according to claim 10, wherein said paraffinic hydrocarbon components comprise on average more than 16 methyl branches per 100 carbon atoms.

25 18. The lubricant basestock composition according to claim 10, wherein the combination of dynamic viscosity, as measured by CCS at -40°C , and kinetic viscosity as measured at 100°C of said liquid hydrocarbon fluid are represented by the formula:

(c) $\text{DV}_{-40^\circ\text{C}} < 2900(\text{KV}_{100^\circ\text{C}}) - 7000$.

30 19. A lubricating oil composition, comprising a liquid hydrocarbon composition having a mixture of paraffinic hydrocarbon components in which the extent of branching, as measured by

the percentage of methyl hydrogens (BI), and the proximity of branching, as measured by the percentage of recurring methylene carbons which are four or more carbons removed from an end group or branch ($\text{CH}_2>4$), are such that:

- (a) $\text{BI} - 0.5(\text{CH}_2>4) > 15$; and
- 5 (b) $\text{BI} + 0.85(\text{CH}_2>4) < 45$; —

as measured over said liquid hydrocarbon composition as a whole; and optionally, effective amounts of lubricating oil additives selected from the group consisting of antioxidants, anti-wear additives, extreme pressure additives, friction modifiers, viscosity index improvers, pour point depressants, detergents, dispersants, corrosion inhibitors, metal deactivators, seal 10 compatibility additives, demulsifiers, anti-foam additives, and mixtures thereof.

20. The lubricating oil composition of claim 19, further comprising a lubricating oil basestock selected from the group consisting of mineral oils, polyalphaolefins, esters, polyalkylenes, alkylated aromatics, hydrocrackates and solvent-refined basestocks.

21. The lubricating oil composition of claim 20, wherein said liquid hydrocarbon 15 composition is present at a concentration level of at least 5 wt% of the total lubricating basestock composition.

Low Temperature Viscosity Comparison

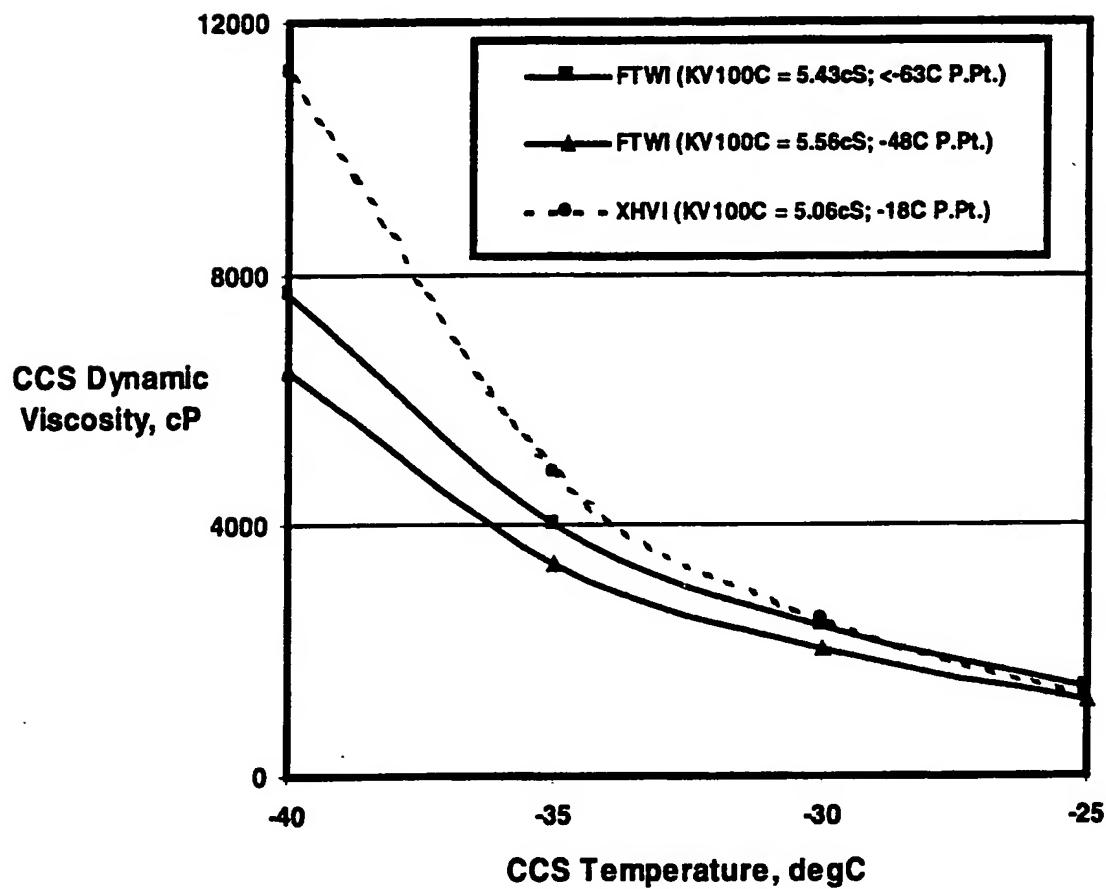


FIG. 1

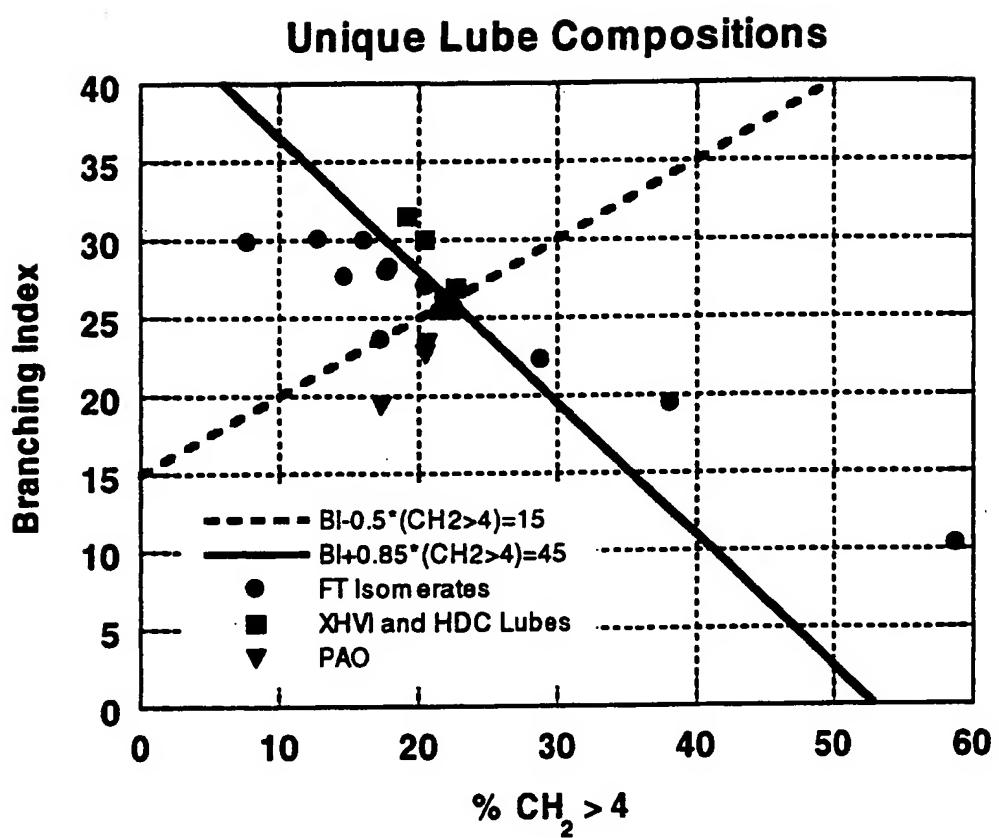
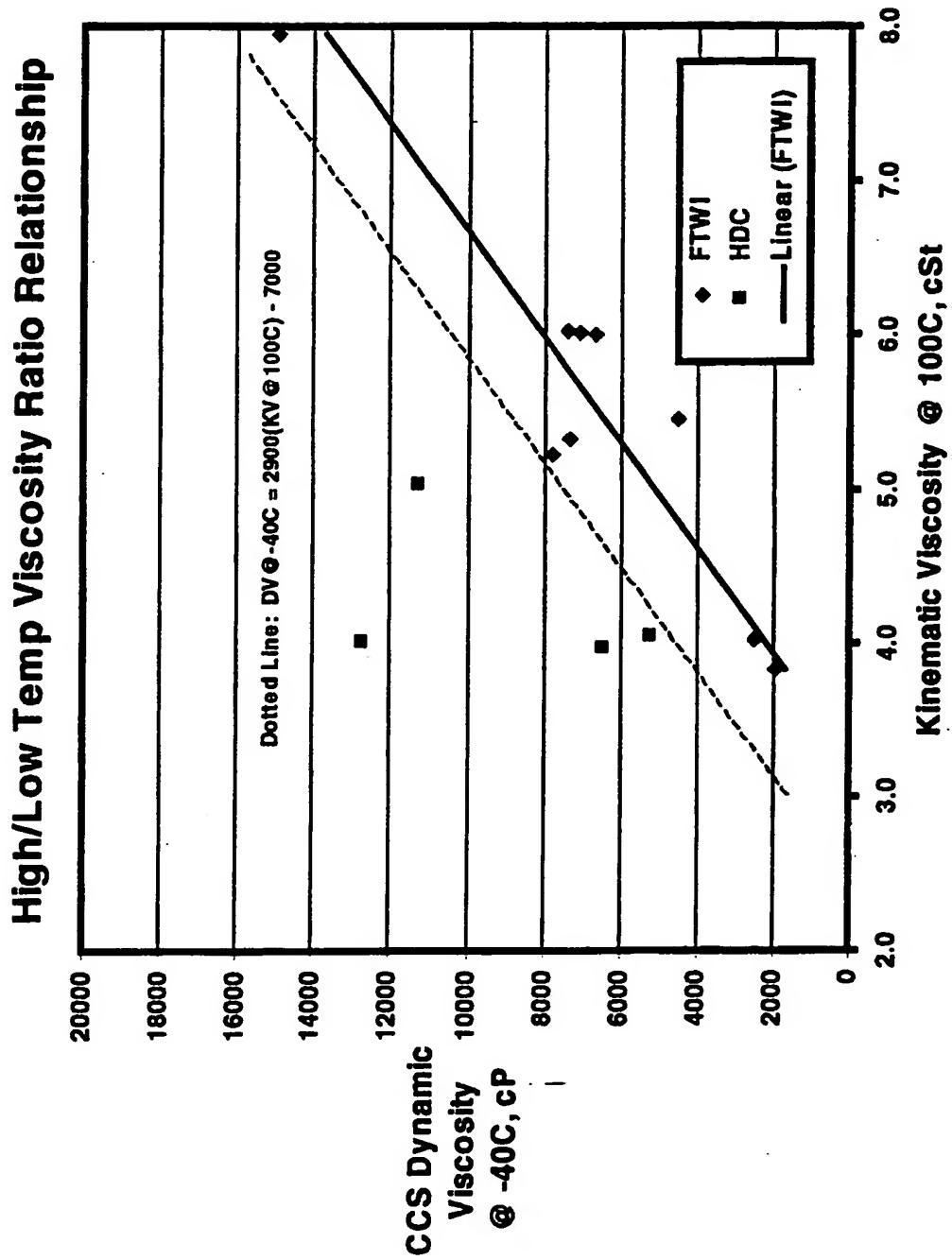


FIG. 2

**FIG. 3**

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/21766

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :C10M 143/08; C10L 3/12; C10L 1/16 C07C 9/16
US CL :585/10, 12, 14, 18

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 585/10, 12, 14, 18

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4,827,064 A (WU) 02 May 1989 (02-05-89). See entire document.	1-21
A	US 5,012,020 A (JACKSON et al) 30 April 1991 (30-04-91). See col 2 line 60 to col 3 line 8.	1-21
Y	US 5,136,118 A (BUCHANAN et al) 04 April 1992 (04-04-92). See entire document.	1-21
Y	US 5,146,022 A (BUCHANAN et al) 08 September 1992 (08-09-92). See entire document.	1-21
Y	US 5,210,347 A (CHEN et al) 11 May 1993 (11-05-93). See entire document.	1-21

 Further documents are listed in the continuation of Box C. See patent family annex.

•	Special categories of cited documents:	
"A"	document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E"	earlier document published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P"	document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

05 FEBRUARY 1999

Date of mailing of the international search report

01 MAR 1999

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

JACQUELINE V. HOWARD

Telephone No. (703) 308-0661

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- BLACK BORDERS**
- IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- FADED TEXT OR DRAWING**
- BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- SKEWED/SLANTED IMAGES**
- COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- GRAY SCALE DOCUMENTS**
- LINES OR MARKS ON ORIGINAL DOCUMENT**
- REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.